

MORDENITE ZEOLITE ALKYLATION CATALYSTS

FIELD OF THE INVENTION

The present invention is directed to a mordenite zeolite catalyst having a controlled macropore structure. The present invention is also directed to catalyst composites comprising mordenite zeolite and a process for preparing the catalyst composites. The present invention is also directed to alkylation of aromatic hydrocarbons using the catalysts and the catalyst composites of this invention. The catalysts and the catalyst composites exhibits reduced deactivation rates during the alkylation process, thereby increasing the life of the catalysts and the catalyst composites as evidenced by the longer alkylation run length times. The catalysts and the catalyst composites of this invention are also capable of being reactivated with a aromatic hydrocarbon flush.

BACKGROUND OF THE INVENTION

It is well known to catalyze the alkylation of aromatics with a variety of Lewis or Bronsted acid catalysts. Typical commercial catalysts include phosphoric acid/kieselguhr, aluminum halides, boron trifluoride, antimony chloride, stannic chloride, zinc chloride, onium poly(hydrogen fluoride), and hydrogen fluoride. Alkylation with lower molecular weight olefins, such as propylene, can be carried out in the liquid or vapor phase. For alkylations with higher olefins, such as C₁₆ olefins, the alkylations are done in the liquid phase, usually in the presence of hydrogen fluoride. Alkylation of benzene with higher olefins is especially difficult, and requires hydrogen fluoride treatment. However, hydrogen fluoride is not environmentally attractive.

The use of the above listed acids is extremely corrosive, thus requiring special handling and equipment. Also, the use of these acids might involve environmental problems. Another problem is that the use of these acids can

1 give less than desirable control on the precise chemical composition of the
2 product produced. Thus, it would be preferable to use a safer, simpler
3 catalyst, preferably in solid state. This simpler process would result in less
4 capital investment, which would result in a less expensive product.

5 Solid crystalline aluminosilicate zeolite catalysts have been known to be
6 effective for the alkylation of aromatics with olefins. Zeolitic materials which
7 are useful as catalysts are usually inorganic crystalline materials that possess
8 uniform pores with diameters in micropore range that is less than
9 20 angstroms. Zeolites occur naturally and may also be prepared
10 synthetically. Synthetic zeolites include, for example, zeolites A, X, Y, L and
11 mordenite. It is also possible to generate metaloaluminophosphates and
12 metalosilicophosphates. Other materials, such as boron, gallium, iron or
13 germanium, may also be used to replace the aluminum or silicon in the
14 framework structure.

15 These zeolite catalyst materials are commercially available as fine crystalline
16 powders for further modification to enhance their catalytic properties for
17 particular applications. Processes for the further modification to enhance
18 catalytic properties of the crystalline zeolite catalysts are well known in the art,
19 such as forming the zeolite catalysts into shaped particles, exchanging the
20 cations in the catalyst matrix, etc.

21 Forming the zeolite powders into shaped particles may be accomplished by
22 forming a gel or paste of the catalyst powder with the addition of a suitable
23 binder material such as a clay, an inorganic compound, or an organic
24 compound and then extruding the gel or paste into the desired form. Zeolite
25 powders may also be formed into particles without the use of a binder.
26 Typical catalyst particles include extrudates whose cross sections are circular
27 or embrace a plurality of arcuate lobes extending outwardly from the central
28 portion of the catalyst particles.

1 One problem with catalyst particles used in fixed bed reactors is catalyst
2 deactivation. In most hydrocarbon conversion processes, including alkylation,
3 the primary catalyst deactivation is caused by coke formation. This catalyst
4 deactivation is a serious problem in the use of zeolite catalysts for alkylation
5 reactions. This deactivation problem is well known in the art and it is well
6 understood that the deactivation mechanism can involve polymerization of the
7 olefin into large molecular species that cannot diffuse out of the pores
8 containing the active sites in the zeolitic material.

9 The use of zeolite catalysts for preparation of alkylated aromatic
10 hydrocarbons is typically conducted by the catalytic alkylation of aromatic
11 hydrocarbons with normal alpha olefins or branched-chain olefins, and
12 optionally a promotor.

13 A number of patents have discussed processes for the preparation of zeolite
14 catalysts and the further shaping and forming of the catalyst particles and
15 extrudates with and without the use of binders. There are also a number of
16 patents disclosing the use of zeolite catalysts for alkylation of aromatic
17 hydrocarbons.

18 U.S. Pat. No. 3,094,383 discloses the preparation of synthetic zeolite
19 materials which upon hydration yield a sorbent of controlled effective pore
20 diameter and in which the sorbent and its zeolite precursor are provided
21 directly in the form of an aggregate.

22 U.S. Pat. No. 3,119,660 discloses a process for making massive bodies or
23 shapes of crystalline zeolites. The patent also discloses methods for the
24 identification of the catalyst materials using X-ray powder diffraction patterns
25 in conjunction with chemical analyses.

26 U.S. Pat. No. 3,288,716 discloses that the high "heavy content" of the
27 alkylated aromatic product can be controlled during the alkylation step and

1 has advantages over distilling the alkylated aromatic product to obtain the
2 desired molecular weight.

3 U.S. Pat. Nos. 3,641,177 and 3,929,672 disclose the technique to remove
4 sodium or other alkali metal ions from zeolite catalysts. The '177 patent also
5 discloses that such removal of the sodium or other alkali metal ions activates
6 the zeolite catalysts for the alkylation of aromatic hydrocarbons with olefins by
7 liquid phase reaction.

8 U.S. Pat. Nos. 3,764,533, 4,259,193 and 5,112,506 disclose the "heavy
9 alkylate" content influences neutral sulfonates and overbased sulfonates. In
10 U.S. Pat. No. 5,112,506, the effect of molecular weight distribution or "heavy
11 alkylate" is shown to influence the performance of both Neutral and HOB
12 sulfonates and the di-alkylate content is shown to influence the rust
13 performance of the corresponding sulfonate in U.S. Pat. No. 3,764,533. In
14 U.S. Pat. No. 4,259,193, a mono-alkylate sulfonate is preferred. U.S. Pat.
15 Nos. 3,288,716; 3,764,533; 4,259,193; and 5,112,506 are hereby
16 incorporated by reference for all purposes.

17 U.S. Pat. No. 3,777,006 discloses the use of nucleating centers for the
18 crystallization of crystalline aluminosilicate zeolites having a size in excess of
19 200 microns and characterized by high strength and excellent adsorptive
20 properties.

21 U.S. Pat. No. 4,185,040 discloses the preparation of highly stable and active
22 catalysts for the alkylation of aromatic hydrocarbons with C₂-C₄ olefins. The
23 catalysts are acidic crystalline aluminosilicate zeolites which exhibit much
24 improved deactivation rates.

25 U.S. Pat. No. 4,764,295 discloses a process for making non-foaming
26 detergent-dispersant lubricating oil additives. The process further involves
27 carbonation for making the products more basic.

1 U.S. Pat. No. 4,891,448 discloses a process for alkylation of polycyclic
2 aromatic compounds in the presence of an acidic mordenite zeolite catalyst
3 having a silica to alumina molar ratio of at least 15:1 to produce a mixture of
4 substituted polycyclic aromatic compounds enriched in the para alkylated
5 isomers.

6 U.S. Pat. No. 5,004,841 discloses a process for alkylation of polycyclic
7 aromatic compounds in the presence of an acidic mordenite zeolite catalyst
8 having a silica to alumina molar ratio of at least 15:1 to produce substituted
9 polycyclic aromatic compounds enriched in the linear alkylated isomers.

10 U.S. Pat. No. 5,118,896 discloses an aromatic alkylation process comprising
11 the steps of contacting a aromatic hydrocarbon feed with an alkylating agent
12 under liquid phase alkylation conditions in the presence of a silica-containing
13 large macropore, small particle size zeolite catalyst, the catalyst having a pore
14 volume of about 0.25 to 0.50 cc/g in pores having a radius of 450 angstroms
15 and a catalyst particle diameter of not more than 1/32 of an inch.

16 U.S. Pat. No. 5,175,135 discloses the use of an acidic mordenite zeolite
17 catalyst for alkylation of aromatic compounds with an alkylating agent having
18 from one carbon atom to eight carbon atoms to produce substituted aromatic
19 compounds enriched in the linear alkylated isomers. The acidic mordenite
20 catalyst is characterized by its silica to alumina molar ratio, its porosity and a
21 Symmetry Index.

22 U.S. Pat. No. 5,191,135 discloses the process for making long-chain alkyl-
23 substituted aromatic compounds from naphthalenes, the process comprising
24 a zeolite alkylation catalyst in the presence of 0.5 to 3.0 weight percent water.
25 The presence of water increases the selectivity for making mono-alkylated
26 products.

1 U.S. Pat. No. 5,198,595 discloses a process for alkylation of benzene or
2 substituted benzene in the presence of an acidic mordenite zeolite catalyst
3 having a silica to alumina ratio of at least 160:1 and a Symmetry Index above
4 about 1.0. A process for the preparation of the catalyst is also disclosed.

5 U.S. Pat. No. 5,243,116 discloses the production of alkylated benzenes by
6 alkylation and/or transalkylation in the presence of an acidic mordenite zeolite
7 catalyst having a silica to alumina molar ratio of at least 30:1 and a specific
8 crystalline structure determined by X-ray diffraction.

9 U.S. Pat. Nos. 5,240,889 and 5,324,877 disclose processes for the
10 preparation of a catalyst composition having alkylation and/or transalkylation
11 activity and wherein the catalyst composition contains greater than 3.5 weight
12 percent water based on the total weight of the catalyst composition and the
13 aromatic alkylation process using said catalyst composition and olefins
14 containing 2 carbon atoms to 25 carbon atoms.

15 U.S. Pat. No. 5,453,553 discloses a process for the production of linear alkyl
16 benzenes which process comprises co-feeding a mixture of benzene, linear
17 olefins and molecular hydrogen in the presence of a zeolite catalyst
18 containing a transition metal under alkylation condition such that the catalyst
19 is not deactivated.

20 U.S. Pat. No. 5,922,922 discloses a process for isomerizing a normal alpha
21 olefin in the presence of an acidic catalyst having a one-dimensional pore
22 system, and then use of the isomerized olefin to alkylate aromatic
23 hydrocarbons in the presence of a second acidic catalyst, which can be
24 mordenite zeolite having a silica to alumina ratio of at least 40 to 1.

25 U.S. Pat. No. 5,939,594 discloses the preparation of a superalkalinized
26 alkylaryl sulfonate of alkaline earth metal. The alkyl group of the alkylaryl
27 sulfonate contains between 14 to 40 carbon atoms and the aryl sulfonate

1 radical of alkaline earth metal is fixed in a molar proportion comprised
2 between 0 and 13% in positions 1 or 2 of the linear alkyl chain.

3 U.S. Pat. No. 6,031,144 discloses a process for reducing the residual olefin
4 content of an alkylation reaction product by removing at least a portion of the
5 non-alkylated single-ring aromatic hydrocarbon and then reacting the
6 remaining alkylation reaction product in the presence of an acidic catalyst
7 such as a molecular sieve or clay.

8 U.S. Pat. No. 6,337,310 discloses the preparation of alkylbenzene from
9 preisomerized normal alpha olefins for making low overbased and high
10 overbased sulfonates having a total base number between 3 and 500. The
11 process uses HF as catalyst or a solid acidic alkylation catalyst, such as a
12 zeolite having an average pore size of at least 6 angstroms.

13 U.S. Pat. No. 6,525,234 discloses a process for alkylating aromatic using a
14 porous crystalline material, e.g., MCM-22 and in situ regenerating the catalyst
15 by use of a polar compound having a dipole moment of at least 0.05 Debyes.

16 It is known that most solid acid catalysts produce high 2-aryl attachment when
17 alkylating with alpha-olefins. See S. Sivasanker, A. Thangaraj, "Distribution of
18 Isomers in the Alkylation of Benzene with Long-Chain Olefins over Solid Acid
19 Catalysts," *Journal of Catalysis*, 138, 386-390 (1992). This is especially true
20 for mordenite zeolite.

21 Two general treatises on zeolite are: Handbook of Molecular Sieves by
22 Rosemarie Szostak (Van Nostrand Reinhold, New York 1992) and Molecular
23 Sieves: Principles of Synthesis and Identification, 2nd Edition, by Rosemarie
24 Szostak (Chapman and Hall, London, UK 1999).

1

SUMMARY OF THE INVENTION

2 The present invention is directed to a mordenite zeolite catalyst having a
3 controlled macropore structure. The present invention is also directed to
4 catalyst composites comprising mordenite zeolite and a process for preparing
5 the catalyst composites. The present invention is also directed to processes
6 for preparation of alkylated aromatic hydrocarbons, which processes comprise
7 the alkylation in the presence of the catalysts and catalyst composites of this
8 invention.

9 The catalysts and the catalyst composites exhibits reduced deactivation rates
10 during the alkylation process, thereby increasing the life of the catalysts and
11 the catalyst composites, as evidenced by the longer alkylation run length
12 times.

13 In particular, the present invention is directed to catalysts having a macropore
14 structure comprising mordenite zeolite having a silica to alumina molar ratio in
15 the range of about 50:1 to about 105:1 and wherein the peak macropore
16 diameter of the catalyst, measured by ASTM Test No. D 4284-03, is less than
17 or equal to about 900 angstroms, and the cumulative pore volume at pore
18 diameters less than or equal to about 500 angstroms, measured by ASTM
19 Test No. D 4284-03, is less than or equal to about 0.30 milliliters per gram,
20 preferably at pore diameters less than or equal to about 400 angstroms less
21 than about 0.30 milliliters per gram, and more preferably at pore diameters
22 less than or equal to about 400 angstroms in the range of about 0.05 milliliters
23 per gram to about 0.18 milliliters per gram.

24

25 The cumulative pore volume of the mordenite zeolite catalysts preferably at
26 pore diameters less than or equal to about 300 angstroms is less than about
27 0.25 milliliters per gram, more preferably at pore diameters less than or equal
28 to about 300 angstroms less than about 0.20 milliliters per gram, and most

1 preferably at pore diameters less than or equal to about 300 angstroms in the
2 range of about 0.08 milliliters per gram to about 0.16 milliliters per gram.

3 Preferably the peak macropore diameter of the above catalysts is in the range
4 of about 400 angstroms to about 800 angstroms, more preferably the peak
5 macropore diameter is in the range of about 400 angstroms to about
6 700 angstroms, and most preferably the peak macropore diameter of the
7 catalyst is in the range of about 450 angstroms to about 600 angstroms.

8

9 The mordenite zeolite of the catalyst of the present invention has a silica to
10 alumina molar ratio of about 50:1 to about 105:1. Preferably the mordenite
11 zeolite has a silica to alumina molar ratio of about 65:1 to about 95:1.

12

13 The catalyst of the present embodiment may be in the form of a tablet.

14

15 A further embodiment of the present invention is directed to a catalyst
16 composite comprising:

17 (a) the mordenite zeolite catalyst of the above invention; and

18 (b) a binder.

19 The binder in step (b) of the above process for making the mordenite zeolite
20 catalyst composite is an inorganic material, preferably the binder is alumina.

21 The mordenite zeolite is present in the above catalyst composite in the range
22 of about 50 weight percent to about 99 weight percent based on the total dry
23 weight of the catalyst composite. Preferably the mordenite zeolite is present
24 in the range of about 60 weight percent to about 90 weight percent based on
25 the total dry weight of the catalyst composite.

1 A further embodiment of the present invention is directed to catalyst
2 composites made by the above process.

3 Yet another embodiment of the present invention is directed to the process for
4 preparing a catalyst composite comprising the steps of:

5 (a) contacting a mordenite zeolite powder having a silica to alumina
6 molar ratio in the range of about 50:1 to about 105:1 with a binder
7 in the presence of volatiles to form a mixture wherein the weight
8 ratio of the mordenite zeolite is range of about 50 to about 99
9 based on the total dry weight of the resulting catalyst composite,
10 and wherein the volatiles in the mixture are in the range of about
11 30 weight percent to about 70 weight percent;

12 (b) shaping the mixture to form a composite;

13 (c) drying the composite; and

14 (d) calcining the composite in a substantially dry environment.

15 In step (a) of the above process, the temperature is typically at least 15°C,
16 preferably the temperature is at least 20°C, and more preferably the
17 temperature is at least 27°C.

18 The above process further comprises addition of an shaping aid in step (a).

19 The shaping in step (b) in the above process preferably comprises extruding.

20 The drying in step (c) in the above process is typically carried out at
21 temperatures in the range of about 100°C to about 200°C.

1 Calcining in step (d) in the above process is typically carried out at
2 temperatures in the range of about 400°C to about 1,000°C in a substantially
3 dry environment.

4 The binder in step (a) of the above process for making the mordenite zeolite
5 composite is an inorganic material, preferably the binder is alumina.

6 The volatiles in step (a) in the process for making the mordenite zeolite
7 composite comprise water and an acid, and preferably the acid is nitric acid.

8 The volatiles in step (a) in the above process for making the mordenite zeolite
9 composite further comprise a polysaccharide.

10 The volatiles in the mixture in step (a) in the process for making the mordenite
11 zeolite composite are preferably in the range of about 40 weight percent to
12 about 60 weight percent of the mixture.

13 In step (a) of the above process, the weight percent of the mordenite zeolite is
14 preferably in the range of about 60 weight percent to about 90 weight percent
15 of the mixture.

16 A further embodiment of the present invention is directed to catalyst
17 composites made by the above process.

18 Another embodiment of the present invention is directed to a process for
19 making an alkylated aromatic composition comprising contacting at least one
20 aromatic hydrocarbon with at least one olefin under alkylation conditions in
21 the presence of a catalyst having a macropore structure comprising mordenite
22 zeolite having a silica to alumina molar ratio in the range of about 50:1 to
23 about 105:1 and wherein the peak macropore diameter of the catalyst,
24 measured by ASTM Test No. D 4284-03, is less than about 900 angstroms
25 and cumulative pore volume at pore diameters less than or equal to about

1 500 angstroms, measured by ASTM Test No. D 4284-03, is equal to or less
2 than about 0.30 milliliters per gram.

3 The above process may further comprise in step (b) the reactivation of the
4 deactivated zeolite catalyst with a suitable solvent flush, preferably the solvent
5 is an aromatic hydrocarbon. More preferably, the aromatic hydrocarbon is
6 benzene.

7 The above process further comprises sulfonating the alkylated aromatic
8 composition.

9 The aromatic hydrocarbon of the above process is benzene, toluene, xylene,
10 cumene, or mixtures thereof. Preferably, the aromatic is benzene or toluene.

11 The olefin in the above process may have from about 4 carbon atoms to
12 about 80 carbon atoms. The olefin may be an alpha olefin, an isomerized
13 olefin, a branched-chain olefin, or mixtures thereof. The alpha olefin or the
14 isomerized olefin may have from about 6 carbon atoms to about 40 carbon
15 atoms, preferably from about 18 carbon atoms to about 28 carbon atoms, and
16 more preferably from about 20 carbon atoms to about 24 carbon atoms. The
17 branched-chain olefin may have from about 6 carbon atoms to about
18 70 carbon atoms, preferably from about 8 carbon atoms to about 50 carbon
19 atoms, and more preferably from about 12 carbon atoms to about 18 carbon
20 atoms.

21 The olefin of the present embodiment may be a partially-branched-chain
22 isomerized olefin having about 6 carbon atoms to about 40 carbon atoms.
23 Preferably, the partially-branched-chain olefin has from about 20 carbon
24 atoms to about 40 carbon atoms.

25 The process of the above embodiment of the present invention for making an
26 alkylated aromatic composition further comprises the step of isomerizing the

1 normal alpha olefin with an isomerizing acidic catalyst before contacting the
2 aromatic with the olefin to prepare an alkyl aromatic product where less than
3 40 weight percent of the alkylated aromatic hydrocarbon is 2-aryl, and at least
4 20 weight percent, preferably at least 75 weight percent of the alkylated
5 aromatic hydrocarbon is a mono-alkylate.

6 The isomerizing acidic catalyst of the above process of the present invention
7 for making an alkylated aromatic composition is preferably the a solid catalyst
8 having at least one metal oxide, which has an average pore size of less than
9 5.5 angstroms. More preferably, that solid catalyst is a molecular sieve with a
10 one-dimensional pore system. As used herein, the average pore size of a
11 catalyst refers only to the pores within the active portion thereof, and does not
12 include pores of any inactive binder or support used therewith.

13 The alkylation process as described above is carried out without the addition
14 of water and using dried aromatic hydrocarbon and olefin feed. It is believed
15 that the presence of water during the alkylation process contributes to an
16 increase in the deactivation of the alkylation catalysts of this invention.

17 The alkylation processes of the above embodiments are further characterized
18 by an increase of at least 50 hours in the alkylation run length time compared
19 to the mordenite zeolite catalysts having a peak macropore diameter greater
20 than 900 angstroms and a cumulative pore volume at pore diameters less
21 than or equal to 300 angstroms greater than 0.30 milliliters per gram,
22 preferably the increase in the alkylation run length time is at least 75 hours,
23 and more preferably the in the alkylation run length time is at least 100 hours.

24 The catalysts and catalyst composites of this invention may be reactivated
25 in situ by use of a suitable flush, such as an aromatic hydrocarbon flush,
26 preferably the flush is with benzene.

1

BRIEF DESCRIPTION OF THE DRAWING

2 Figure 1 is a graph showing the reactivation of Catalyst Composite 3.
3 Preparation of Catalyst Composite 3 is described in Example 4 and its
4 characteristics are given in Tables I and II. The data used to generate the
5 graph in Figure 1 is given in Table III and was collected in an alkylation
6 reaction conducted as described in Example 7. The inlet temperature, which
7 is the temperature of the feed entering the reactor before the reaction
8 exotherm has developed, is also shown in the graph.

9

DETAILED DESCRIPTION OF THE INVENTION

10

DEFINITIONS

11 The term "alkylate" means an alkylated aromatic hydrocarbon.

12 The term "2-aryl content" is defined as the percentage of total alkylate (the
13 alkylate species in which the alkyl chain derived from the olefin employed in
14 the present alkylation process is attached to the aromatic ring) that is
15 comprised of those chemical species in which the attachment of the alkyl
16 chain to the aromatic ring is at the 2-position along the alkyl chain.

17 The term "binder" means any suitable inorganic material which can serve as
18 matrix or porous matrix to bind the zeolite particles into a more useful shape.

19 The term "branched-chain olefins" means olefins derived from the
20 polymerization of olefin monomers higher than ethylene and containing a
21 substantial number of branches wherein the branches are alkyl groups having
22 from about one carbon atom to about 30 carbon atoms. Mixtures of ethylene
23 and higher olefins are also contemplated.

24 The term "calcining" as used herein means heating the catalyst in a
25 substantially dry environment to about 400°C to about 1,000°C.

1 The term “cumulative pore volume” obtained by Mercury Intrusion Porosimetry
2 as used herein refers to that part of the total volume in milliliters per gram
3 derived from the graphical, cumulative pore volume distribution, measured by
4 Section 14.1.6 of ASTM D 4284-03, or the corresponding tabular presentation
5 of the same data between defined upper and lower pore diameters. When no
6 lower diameter limit is defined, the lower limit is the lowest detection limit or
7 lowest radius measured by Section 14.1.6 of ASTM D 4284-03.

8 The terms “dry basis”, “anhydrous basis”, and “volatiles-free basis” shall refer
9 to the dry weight of catalyst composite or raw materials expressed on a metal
10 oxides basis such as $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$.

11 The term “flush” as used herein means contacting the deactivated catalysts
12 and catalyst composites of this invention in the reactor with a suitable solvent,
13 such as an aromatic hydrocarbon for reactivation of the catalysts and catalyst
14 composites.

15 The term “loss-on-ignition (LOI)” as used herein means the percent weight
16 loss of the zeolite composite or raw material samples when they are heated to
17 538°C for 1 hour. When the temperature is greater than or equal to about
18 538°C, the “loss-on-ignition” approximates the percent volatiles.

19 The terms “macropore”, “mesopore”, and “micropore” as used herein follow
20 the definitions set forth by the International Union of Pure and Applied
21 Chemistry (IUPAC), Division of Physical Chemistry, in Manual of Symbols and
22 Terminology for Physicochemical Quantities and Units, Appendix II
23 Definitions, Terminology and Symbols in Colloid and Surface Chemistry
24 Part 1, Adopted by the IUPAC Council at Washington, D.C., USA, on 23 July,
25 1971. Pores with widths or diameters exceeding ~50 nanometers
26 (500 angstroms) are called “macropores”. Pores with widths or diameters not
27 exceeding ~2.0 nanometers (20 angstroms) are called “micropores”. Pores of

1 intermediate size (2.0 nanometers < width or diameter ≤ 50 nanometers) are
2 called "mesopores".

3 The term "Mercury Intrusion Porosimetry" refers to the ASTM Test
4 No. D 4284-03 used to determine pore volume distribution of catalysts by
5 Mercury Intrusion Porosimetry. Mercury pore distribution was measured ,
6 using a Quantachrome Scanning Mercury Porosimeter Model SP-100. The
7 software version used by the instrument is V2.11 (dated 10/27/93). Surface
8 tension used in the calculation is 473 dynes per centimeter and the contact
9 angle is 140 degrees.

10 The terms "normal alpha olefin" and "linear alpha olefin" mean those
11 straight-chain olefins without a significant degree of alkyl branching in which
12 the carbon to carbon double bond resides primarily at the end or "alpha"
13 position of the carbon chain, i.e., between C₁ and C₂. Normal alpha olefins
14 are derived from polymerization of ethylene.

15 The term "normal alpha olefin isomerization" means the conversion of normal
16 alpha olefins into isomerized olefins having a lower alpha olefin content (the
17 double bond is between C₁ and C₂), higher internal olefin content (the double
18 bond is in positions other than between C₁ and C₂), and optionally a higher
19 degree of branching.

20 The term "partially-branched chain olefin" is defined as the olefin product of
21 isomerization of normal alpha olefins wherein the degree of branching is
22 higher than in the starting normal alpha olefins.

23 The term "peak macropore diameter" as used herein means the peak
24 diameter (i.e., the diameter within the macropore region at which the
25 differential plot of pore size distribution, as defined by section 14.2, reaches a
26 maximum) in the macropore range determined by ASTM Test No. 4284-03 for
27 the macropore peak in the catalysts of the present invention.

1 The term "peptizing" means the dispersion of large aggregates of binder
2 particles, including hydrated aluminas, into much smaller primary particles by
3 the addition of acid.

4 The term "percent volatiles" as used herein means the difference between the
5 actual weight of the catalyst composite or the raw materials and the weight of
6 the material on a substantially dry, anhydrous, or volatiles-free basis,
7 expressed as a percentage of the actual sample weight.

8 The term "SAR" or "silica to alumina ratio" refers to the molar ratio of silicon
9 oxide to aluminum oxide; mol SiO₂:mol Al₂O₃.

10 The term "sufficient water to shape the catalyst material" means quantity of
11 water required to make an acid peptized mixture of zeolite and alumina
12 powders into an extrudable mass.

13 The term "tableting" as used herein refers to the process of forming a catalyst
14 aggregate from zeolite powder or a mixture of zeolite and binder powders by
15 compressing the powder in a die.

16 The term "total pore volume" obtained by Mercury Intrusion Porosimetry as
17 used herein refers to the total pore volume in milliliters per gram derived from
18 the graphical, cumulative pore volume distribution (Section 14.1.6 of ASTM
19 D 4284-03) or the corresponding tabular presentation of the same data.

20 As used herein, all percentages are weight percent, unless otherwise
21 specified.

22 As noted above, the present invention is directed to catalysts having a
23 controlled macropore structure comprising mordenite zeolite. The catalysts of
24 the present invention were characterized by pore volume distribution obtained
25 by Mercury Intrusion Porosimetry, ASTM Test No. D 4284-03. Mercury
26 Intrusion Porosimetry provides a graph of cumulative pore volume (pv) versus

1 pore diameter (pd). Mercury Intrusion Porosimetry also is used to determine
2 the macropore peak diameter from the derivative, Δp_v divided by
3 Δp_d . The graphs are used to characterize the catalysts of the
4 present invention.

5 Mordenite zeolitic catalysts and catalyst composites of the present invention
6 when used in alkylation of aromatic hydrocarbons with olefins exhibited a
7 reduction in deactivation rates as measured by increase in alkylation run
8 length times compared to zeolitic catalysts known in the prior art. This result
9 was unexpected, since it had previously been believed that increasing the
10 surface area of the catalyst would increase its activity, but was likely to also
11 increase deactivation rates. Relative deactivation rates were determined for
12 the catalysts of the present invention under standard alkylation reactions
13 conditions. Results of the deactivation experiments are given in Table II. The
14 mordenite zeolite catalyst composites of the present invention exhibit
15 reduction in deactivation rates evidenced by substantially longer run length
16 times compared to mordenite zeolite catalysts that do not have the macropore
17 structure and the pore volume distribution of the mordenite zeolite catalyst
18 composites of the present invention.

19 The mordenite zeolite catalysts and catalyst composites of the present
20 invention also exhibited unexpected results in their ability to be reactivated
21 with a flush using a suitable solvent, such as an aromatic hydrocarbon,
22 preferably benzene. This was surprising since generally prior art zeolite
23 alkylation catalysts cannot be easily reactivated in situ once they are
24 deactivated. Once the prior art zeolite alkylation catalysts are completely
25 deactivated, the reactor bed must be changed to remove the deactivated
26 zeolite catalysts. In the case of the mordenite zeolite catalysts and catalyst
27 composites of the present invention, all that is required is that at the end of an
28 alkylation run the olefin feed stream is stopped while the aromatic
29 hydrocarbon continues to be flushed through the reactor for a sufficient
30 number of hours. Economically, the use of the mordenite zeolite catalysts

1 and catalyst composites of the present invention for alkylation of aromatic
2 hydrocarbons with olefins is highly desirable.

3 The mordenite zeolitic catalysts composites may be prepared using mordenite
4 zeolite CBV 90A® available from Zeolyst International having a nominal silica
5 to alumina ratio of 90:1. Any available similar mordenite zeolite may be used
6 for preparing the mordenite zeolite catalyst composites of the present
7 invention. It is believed that mordenite zeolite having a silica to alumina ratio
8 between about 50:1 and about 105:1 may be used for the preparation of the
9 mordenite catalyst composites of the present invention.

10 The catalysts of the present invention may be shaped or formed into tablets,
11 extrudates or any other shape. The preparation of extrudates requires the
12 presence of a binder, such as alumina. The tabletted catalysts do not require
13 the presence of a binder. The crystalline mordenite zeolite powder may be
14 compressed to form a tablet.

15 The alkylation reaction may be carried out by any conventionally known
16 process. The alkylation process using the mordenite zeolite catalysts and
17 catalyst composites of the present invention is conducted in the absence of
18 water. The aromatic hydrocarbon is reacted with one or more olefins in the
19 presence of a catalyst of the present invention under alkylation reaction
20 conditions. The aromatic hydrocarbon may be single-ring or double-ring,
21 preferably the aromatic hydrocarbon is a single-ring. The aromatic
22 hydrocarbon may be an alkylated aromatic, such as a mono-alkylated
23 aromatic, wherein the alkyl group has from about 4 carbon atoms to about
24 80 carbon atoms. When the aromatic hydrocarbon used is a mono-alkylated
25 aromatic, the product of the alkylation reaction is a di-alkylated aromatic.

26 The olefins useful for alkylation of the aromatic hydrocarbons may be
27 linear-chain or branched-chain having from about 4 carbon atoms to about
28 80 carbon atoms. In addition, normal alpha olefins may be isomerized to

1 obtain partially-branched-chain olefins for use in alkylation reaction of the
2 present invention. These resulting partially-branched-chain olefins may be
3 alpha-olefins, beta-olefins, internal-olefins, tri-substituted olefins, and
4 vinylidene olefins.

5 Procedure for Isomerization of Normal Alpha Olefins

6 The isomerization process may be carried out in batch or continuous mode.
7 The process temperatures can range from 50°C to 250°C. In the batch mode,
8 a typical method is to use a stirred autoclave or glass flask, which may be
9 heated to the desired reaction temperature. A continuous process is most
10 efficiently carried out in a fixed bed process. Space rates in a fixed bed
11 process can range from 0.1 to 10 or more weight hourly space velocity.

12 In a fixed bed process, the isomerization catalyst is charged to the reactor and
13 activated or dried at a temperature of at least 150°C under vacuum or flowing
14 inert, dry gas. After activation, the temperature of the isomerization catalyst is
15 adjusted to the desired reaction temperature and a flow of the olefin is
16 introduced. The reactor effluent containing the partially-branched, isomerized
17 olefin is collected. The resulting partially-branched, isomerized olefin contains
18 a different olefin distribution (alpha olefin, beta olefin; internal olefin,
19 tri-substituted olefin, and vinylidene olefin) and branching content than the
20 unisomerized olefin.

21 Procedure for Alkylation of Aromatic Hydrocarbons

22 Alkylation of aromatic hydrocarbons with normal alpha olefins, partially-
23 branched-chain isomerized olefins, and branched-chain olefins may be
24 carried out by any method known by a person skilled in the art.

25 The alkylation reaction is typically carried out with an aromatic and an olefin in
26 molar ratios from 1:2 to 25:1. Process temperatures can range from about

1 100°C to about 250°C. As the olefins have a high boiling point, the process is
2 preferably carried out in the liquid phase. The alkylation process may be
3 carried out in batch or continuous mode. In the batch mode, a typical method
4 is to use a stirred autoclave or glass flask, which may be heated to the
5 desired reaction temperature. A continuous process is most efficiently carried
6 out in a fixed bed process. Space rates in a fixed bed process can range from
7 0.01 to 10 or more weight hourly space velocity.

8 In a fixed bed process, the alkylation catalyst is charged to the reactor and
9 activated or dried at a temperature of at least 150°C under vacuum or flowing
10 inert, dry gas. After activation, the alkylation catalyst is cooled to ambient
11 temperature and a flow of the aromatic hydrocarbon compound is introduced,
12 optionally toluene. Pressure is increased by means of a back pressure valve
13 so that the pressure is above the bubble point pressure of the aromatic
14 hydrocarbon feed composition at the desired reaction temperature. After
15 pressurizing the system to the desired pressure, the temperature is increased
16 to the desired reaction temperature. A flow of the olefin is then mixed with the
17 aromatic hydrocarbon and allowed to flow over the catalyst. The reactor
18 effluent comprising alkylated aromatic hydrocarbon, unreacted olefin and
19 excess aromatic hydrocarbon compound is collected. The excess aromatic
20 hydrocarbon compound is then removed by distillation, stripping, evaporation
21 under vacuum, or any other means known to those skilled in the art.

22 Reactivation of Deactivated Mordenite Zeolite Catalysts and Composites

23 Once the mordenite zeolite catalysts and catalyst composites are completely
24 deactivated, the alkylation reaction slows down or stops because access to
25 the active sites is restricted by large molecular species formed by olefin
26 polymerization that cannot diffuse out of pores containing the active sites in
27 the zeolitic material. However, reactor bed need not be changed to remove
28 the deactivated mordenite zeolite catalysts and catalyst composites. The
29 deactivated mordenite zeolite catalysts and catalyst composites are

1 reactivated at the end of an alkylation run by stopping the olefin feed stream
2 to the reactor and permitting the aromatic hydrocarbon stream to continue to
3 be flushed through the reactor for a sufficient time, typically from about
4 16 hours to about 60 hours.

5 EXAMPLES

6 Preparation of Mordenite zeolite Alkylation Catalyst Composites

7 Example 1

8 Preparation of Comparative Catalyst Composite A

9 Mordenite zeolite catalyst composites were prepared by the following method:

10 Loss-on-ignition (LOI) was determined for a sample of a commercially
11 available mordenite zeolite CBV 90A®, available from Zeolyst International,
12 with a silica to alumina molar ratio of 90:1, by heating the sample to 538°C for
13 1 hour. The LOI obtained was 11.56 weight % and provided the percent
14 volatiles in the mordenite zeolite powder being used. The LOI of a
15 commercial sample of Catapal B® hydrated aluminum oxide available from
16 Vista Chemical Company was determined by heating the sample to 538°C for
17 1 hour and was 26.01 weight %. Next, based on the results obtained from the
18 LOI, 588 grams of mordenite zeolite powder and 175.7 grams of alumina
19 powder were weighed out to give a total of 520 grams of mordenite zeolite
20 powder and 130 grams of alumina powder on a volatile-free basis.

21 The two dry powders were manually mixed in a plastic bag and then added to
22 a Baker Perkins mixer and dry mixed for 3 minutes. The amount of
23 concentrated (70.7%) nitric acid to give 0.7 weight % (based on 100% nitric
24 acid) of the dry weight of the zeolite and the alumina powders was calculated
25 to be 12.9 grams. This amount of 70.7% nitric acid was weighed out and
26 dissolved in 294.3 grams of deionized water.

1 The total amount of water and 70.7% nitric acid needed to obtain a final
2 concentration of approximately 42% total volatiles was calculated as follows.
3 Volatiles in the mordenite zeolite powder are 68 grams (588 gram total
4 weight – 520 grams dry weight). Volatiles in the alumina powder are
5 45.7 grams (175.7 grams total weight – 130 grams dry weight). Nitric acid
6 solution is considered to be 100% volatiles. Thus, if all the above raw
7 materials were combined, the volatiles would be 420.9 grams. To give a
8 mixture of 650 grams (520 grams zeolite and 130 grams alumina dry basis)
9 dry powder with 42% volatiles, the total weight of the mixture must be
10 1120.7 grams. Thus, an additional 49.8 of deionized water must be added.

11 To the powders in the mixer, 50 grams of deionized water were added over a
12 period of 17 minutes using a peristaltic pump. The mixer was then stopped so
13 that the walls of the mixer could be scraped down. Mixing was then resumed
14 and the solution of nitric acid in water was added over 10 minutes using the
15 peristaltic pump. At the end of acid addition, the temperature of the wet
16 mixture was 78°C. Mixing was continued for a total time of 40 minutes, with
17 occasional holds to allow for scraping the sides of the mixer. At the end of the
18 mixing period, the wet mixture consisted of large smooth clumps and the wet
19 mixture temperature was 42°C. At this point, the volatiles were
20 41.45 weight %.

21 The wet mixture was extruded through 1.27 millimeter, asymmetric quadrilobe
22 die inserts, in a Ram extruder. The wet long cylindrical strands were dried at
23 121°C for 8 hours. The long cylindrical strands were then broken to give
24 extrudates with length to diameter ratio of 2:3. The extrudates were sieved
25 and the portion larger than 1.7 millimeters was retained.

26 The extrudates were then calcined in a substantially dry environment in a
27 muffle furnace using the following temperature program:

1 The extrudates are heated to 593°C over two hours, then held at 593°C for
2 1.8 hours and next cooled to 204°C. A total of 1681 grams of extrudates were
3 obtained.

4 Mercury Intrusion Porosimetry showed the extrudates to have a peak
5 macropore diameter of 1000 angstroms and a cumulative pore volume at
6 diameters less than 300 angstroms of 0.1587 ml/gram.

7 Example 2

8 Preparation of Catalyst Composite 1

9 Mordenite zeolite catalyst composite was prepared following the procedure
10 used in Example 1 above, with the following exceptions:

11 Volatiles of the mordenite zeolite powder and alumina powder were
12 11.63 weight % and 27.54 weight %, respectively. Corresponding mordenite
13 zeolite and alumina powders were 1176.9 grams and 358.8 grams,
14 respectively. Concentrated nitric acid, 25.8 grams, was dissolved in
15 600 grams deionized water. The powders were dry mixed for 10 minutes and
16 80.3 grams of water was added over 15 minutes. The acid solution was
17 added over 10 minutes at which point the temperature of the mixture was
18 23°C. The steam/water mixer was adjusted to give a jacket temperature of
19 48°C. Mixing was continued for 30 minutes. At this point, the mixture was too
20 pasty, so mixing was continued for 20 minutes with the mixer cover off.
21 Volatiles were 40.41 weight % at extrusion time. The mixture was then
22 extruded, dried, sized and calcined in a substantially dry environment.

23 Mercury Intrusion Porosimetry showed the peak macropore diameter to be
24 574 angstroms and the cumulative pore volume at diameters less than
25 300 angstroms to be 0.1661 ml/gram.

1
2

Example 3

Preparation of Catalyst Composite 2

3 This catalyst composite was made by the procedure described in Examples 1
4 and 2 above with the following exceptions:

5 Volatiles of the zeolite powder and alumina powder were 11.63 weight % and
6 27.54 weight %, respectively. Corresponding amounts of zeolite and alumina
7 powders were 1176.9 grams and 358.8 grams, respectively. The acid
8 solution was made from 25.8 grams of 70.7% nitric acid and 600 grams of
9 deionized water. Added water was 80.3 grams. After 10 minutes of dry
10 mixing the powders, water was added over 15 minutes. Next, the acid
11 solution was added over 10 minutes, which point the temperature of the
12 mixture was 48°C. Mixing was continued for 30 minutes. At this time, the
13 mixture was too pasty, so mixing was continued for 20 minutes with the mixer
14 cover off. Volatiles were 40.41 weight % at extrusion time. After extruding,
15 drying, sizing, and calcining in a substantially dry environment, Mercury
16 Intrusion Porosimetry showed the peak macropore diameter to be
17 768 angstroms and the cumulative pore volume at diameters less than
18 300 angstroms to be 0.1617 ml/gram.

19
20

Example 4

Preparation of Catalyst Composite 3

21 Mordenite zeolite catalyst composite was prepared following the procedure
22 used in Example 1 above, with the following exceptions:

23 Volatiles of the mordenite zeolite powder and alumina powder were
24 10.79 weight % and 25.72 weight %, respectively. Corresponding mordenite
25 zeolite and alumina powders were 582.91 grams and 175.03 grams,
26 respectively. Concentrated nitric acid, 12.9 grams, was dissolved in
27 300 grams deionized water. The powders were dry mixed for 10 minutes and

1 179.12 grams of water was added over 11 minutes. The acid solution was
2 added over 9 minutes. At this point, the mixture had a thick liquid consistency
3 and the temperature of the mixture was 23°C. Heat was applied to the mixer
4 to raise the temperature to 46°C. A stream of air was injected into the mixing
5 chamber to dry the mixture. After mixing for 40 minutes under these
6 conditions, the volatiles were 42.55% and the mixture looked rubbery. Mixing
7 was continued for 10 minutes without added heat or air. At this point, the
8 mixture looked rubbery and wet. Mixing was continued for 25 minutes with a
9 stream of air at which time the mixture was still rubbery and the temperature
10 of the mixture was 41°C. Volatiles were 41.34 weight %. Mixing was
11 continued for an additional 20 minutes with application of heat. The
12 temperature of the mixture was 47°C and the volatiles were 39.93% at this
13 time. The wet mixture had a clay like consistency. The mixture was then
14 extruded through a 1/16 of an inch, asymmetric quadrilobe die inserts, in a
15 Ram extruder, dried, sized and calcined in a substantially dry environment.

16 Mercury Intrusion Porosimetry showed the peak macropore diameter to be
17 645 angstroms and the cumulative pore volume at diameters less than
18 300 angstroms to be 0.1617 ml/gram.

19 Example 5
20 Preparation of Catalyst Composite 4

21 Mordenite zeolite catalyst composite was prepared following the procedure
22 used in Example 1 above, with the following exceptions:

23 Volatiles of the mordenite zeolite powder and alumina powder were
24 12.04 weight % and 26.98 weight %, respectively. Corresponding mordenite
25 zeolite and alumina powders were 1182.2 grams and 356.1 grams,
26 respectively. Concentrated nitric acid, 25.8 grams, was dissolved in
27 600 grams deionized water. The powders were dry mixed in a plastic bag for
28 2 minutes and then dry mixed in the Baker-Perkins mixer for 10 minutes

1 before 288.7 grams of water was added over 15 minutes. The acid solution
2 was added over 10 minutes. At this point, the mixture had a consistency of a
3 thick liquid and the temperature of the mixture was 21°C. Heat was applied to
4 the mixer to raise the jacket temperature to 46°C. A stream of air was
5 injected into the mixing chamber to dry the mixture. After mixing for
6 40 minutes under these conditions, the volatiles were 44.73% and the
7 temperature was 36°C. Mixing was continued for 10 minutes at which point
8 the temperature of the mixture was 39°C and the mixture looked rubbery.
9 After an additional mixing for 25 minutes, the mixture formed large clumps
10 and mixed well. Mixing was continued for an additional 2 minutes without a
11 stream of air. At this point, the temperature of the mixture was 41°C and the
12 volatiles were 38.99% at this time. The wet mixture had a clay-like
13 consistency. The mixture was then extruded through a 1.27 millimeters,
14 asymmetric quadrilobe die inserts, in a Ram extruder, dried, sized and
15 calcined in a substantially dry environment.

16 Mercury Intrusion Porosimetry showed the peak macropore diameter to be
17 570 angstroms and the cumulative pore volume at diameters less than
18 300 angstroms to be 0.1711 ml/gram.

19 The Mercury Intrusion Porosimetry results for the mordenite zeolite catalyst
20 composites of Examples 1-5 are given below in Table I.

21 Table I

Catalyst Composite	Mercury Intrusion Porosimetry Properties		
	Total PV* (ml/gram)	PV <300 angstroms** (ml/gram)	Macropore peak diameter (angstroms)
Comparative A***	0.462	0.1587	1000
1	0.344	0.1661	574
2	0.346	0.1617	768
3	0.329	0.1617	645
4	0.318	0.1711	570

- 1 * Total pore volume.
2 ** Total pore volume at diameters less than or equal to 300 angstroms.
3 *** Catalyst Composite A was used as a comparative catalyst composite for
4 obtaining deactivation rates of Catalysts Composites 3 and 4. The
5 temperature during binding and mixing of the mordenite zeolite and the binder
6 was not adjusted between 45°C and 50°C for the preparation of the
7 Comparative Catalyst Composite A. The temperature during binding and
8 mixing of the mordenite zeolite and the binder was adjusted between 45°C
9 and 50°C for the preparation of the Catalyst Composites 1-4.

10 Example 6
11 Preparation of Isomerized Normal Alpha Olefins

12 Typically, isomerization of normal alpha olefins is carried out as described
13 below:

14 C₂₀-C₂₄ normal alpha olefin with the following composition was used for this
15 Example:

- 16 Alpha olefin 89.1%
17 Beta olefin 0.5%
18 Internal olefin 1.4%
19 Tri-substituted olefin 0.2%
20 Vinylidene olefin 9.5% (determined by carbon nuclear magnetic
21 resonance spectroscopy)
22 Branched-chain olefin 11% (determined by infra red spectroscopy)
23

24 The normal alpha olefin was pumped up-flow through a fixed-bed reactor
25 (570 millimeters high and with an inside diameter of 22.3 millimeters)
26 containing 65 grams of solid olefin isomerization. The reactor was operated
27 isothermally at 160°C at a liquid to hourly space velocity of 0.5 per hour and at
28 atmospheric pressure.

1 The reactor effluent containing the partially branched, isomerized olefin is
2 collected. The resulting partially-branched, isomerized olefin contains a
3 different olefin distribution (alpha-olefin, beta-olefin; internal-olefin,
4 tri-substituted-olefin and vinylidene-olefin) and branching content than the
5 un-isomerized olefin.

6 Example 7
7 Preparation of alkylbenzene compositions

8 Typically, alkylation of aromatic hydrocarbons with normal alpha olefins,
9 partially-branched-chain isomerized olefins and branched-chain olefins was
10 carried out as described below:

11
12 A fixed bed reactor was constructed from 15.54 millimeters Schedule 160
13 stainless steel pipe. Pressure in the reactor was maintained by an
14 appropriate back pressure valve. The reactor and heaters were constructed
15 so that adiabatic temperature control could be maintained during the course of
16 alkylation runs. A bed of 170 grams of 850 micrometer to 2 millimeters
17 Alundum particles was packed in the bottom of the reactor to provide a pre-
18 heat zone. Next, 100 grams of Catalyst Composite 3 was charged to the fixed
19 bed reactor. Finally, void spaces in the catalyst bed were filled with
20 309 grams of 150 micrometers Alundum particles interstitial packing. The
21 reactor was gently vibrated while charging catalyst and alundum to ensure a
22 high packed bulk density. After charging, the reactor was closed, sealed, and
23 the pressure was tested.

24
25 The alkylation catalyst was then heated to 200°C under a 20 liters per hour
26 flow of nitrogen measured at ambient temperature and pressure and
27 dehydrated for 23 hours at 200°C. The catalyst bed was then cooled to 100°C
28 under nitrogen. Benzene was then introduced into the catalytic bed in an
29 up-flow manner at a flow rate of 200 grams per hour. Temperature (under
30 adiabatic temperature control) was increased to a start-of-run inlet

1 temperature of 154°C (measured just before the catalyst bed) and the
2 pressure was increased to 12.66 atmospheres.

3

4 When temperature and pressure had lined out at desired start-of-run
5 conditions of 154°C and 12.66 atmospheres, a feed mixture, consisting of
6 benzene and C₂₀₋₂₄ NAO at a molar ratio of 15:1 and dried over activated
7 alumina, was introduced in an up-flow manner at 200 grams per hour. As the
8 feed reached the catalyst in the reactor, reaction began to occur and internal
9 catalyst bed temperatures increased above the inlet temperature. After about
10 8 hours on-stream, the reactor exotherm was 20°C. In the first 57 hours
11 on-stream, the olefin conversion decreased from 100% to 98.8% (Run
12 Period 1). At this point, the catalyst bed was flushed with benzene at
13 200 grams per hour during 18 hours. Following the benzene flush, the
14 benzene and olefin feed flow was resumed. Inlet temperature was increased
15 to 162°C at 57 run hours. Feed was continued until 351 run hours (Run
16 Period 2 from 57 to 351 run hours). Olefin conversion was initially 98.9%
17 during Run Period 2 but declined to 98.1% at 321 run hours and further to
18 95.3% at 351 run hours. A second benzene flush was performed at 351 run
19 hours during 17 hours. After the second benzene flush, feed flow was
20 resumed again to start Run Period 3. Feed was continued until 550 run
21 hours. Olefin conversion was initially 98.5% but declined to 98.3% at 519 run
22 hours and to 97.0% at 550 run hours. A third benzene flush was done during
23 a weekend. Feed flow was resumed after the third benzene flush to begin
24 Run Period 4. At the beginning of Run Period 4, olefin conversion was 98.8%
25 and at 942 run hours the olefin conversion was 98.4%. The run was stopped
26 after 942 hours on-stream but could have continued longer.

27

28 Alkylated aromatic hydrocarbon products containing excess benzene were
29 collected during the course of the run. After distillation to remove excess
30 aromatic hydrocarbon, analysis showed that greater than 97% conversion of
31 olefin was achieved during most of the course of the run.

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Table II

Catalyst Composite	Temperature (°C)	Silica: Alumina Molar Ratio	Zeolite (%)	Mercury Intrusion Porosimetry			Alkylation Run Length (hours)
				Total PV* (ml/gram)	PV <300 Å (ml/gram)	Peak Macropore Diameter, Å	
3	162	90	80	0.329	0.166	645	293
4	166	90	80	0.318	0.162	570	200
A	170	90	80	0.361	0.159	1000	30

2

3

Example 9

4

Procedure for the Reactivation of Deactivated Catalysts

5

In Alkylation reactions

6

7 Catalyst Composite 3 prepared in Example 4 was used for conducting the
8 reactivation experiments. Comparative Catalyst Composite A prepared in
9 Example 1 was used for comparison in the reactivation experiments.
10 Characteristics obtained by Mercury Intrusion Porosimetry for all three
11 catalysts are shown above in Table II.

12 The alkylation reactions for reactivation of the deactivated alkylation catalysts
13 and catalyst composites of this invention were conducted as described above
14 in Example 7.

15 The inlet temperature was recorded at the start of the alkylation reaction. The
16 inlet temperature is the temperature of the feed entering the reactor before the
17 reaction exotherm has developed. Deactivation of Catalyst Composite 3 and
18 Comparative Catalyst Composite A was observed when the position of the
19 exotherm moved away from the inlet zone, of the reactor. Once the Catalyst
20 Composites were completely deactivated, the alkylation reaction was stopped
21 by stopping the flow of the olefin feed to the reactor and the reactor was
22 flushed with benzene by continuing the flow of the benzene feed for about 16
23 hours to about 60.

At the end of the benzene flush, the alkylation reaction was again started by beginning the flow of the olefin feed and the alkylation reaction was allowed to proceed until the position of the exotherm again moved away from the inlet zone of the reactor. Two reactivation experiments were run with Catalyst Composite 3, which was reactivated four and two times, respectively, with a benzene flush. Comparative Catalyst A was flushed once with benzene for 43 hours, a much longer period than in the case of Catalyst Composite 3, without being reactivated.

Table III below and Figure 1 show the reactivation data collected during the alkylation reactions conducted as in Example 9.

Table III

Experiment	Catalyst Composite	Run Number	Inlet Temperature (°C)	Alkylation Run Time (hours)	Benzene Flush After Run (hours)
1	3	1	154	57 *	18
1	3	2	162	294	17
1	3	3	170	198	Weekend end ****
1	3	4	172	363	16
1	3	5	172	30 **	--
2	3	1	154	184	25
2	3	2	174	96 ***	43
2	3	3	190	217	--
3	Comparative A	1	176	44	43
3	Comparative A	2	159	24	--

* The concentration of the unreacted olefin was observed to increase rapidly which was presumed to indicate deactivation of Catalyst Composite 3. A benzene flush was conducted to reactivate Catalyst Composite 3.

1 ** The experiment was conducted to determine whether a shorter period of
2 benzene flush, 16 hours, would be sufficient to reactivate Catalyst
3 Composite 3. The alkylation run was stopped after 30 hours, but it is believed
4 that the alkylation run could have been allowed to run for a longer period of
5 time.

6 *** Comparative Catalyst A was observed to deactivate very rapidly. A
7 benzene flush of 43 hours did not reactivate Comparative Catalyst A.

8 **** The benzene flush was started on Friday evening by stopping the flow of
9 the olefin feed to the reactor and allowed to continue until the following
10 Monday morning, at which time the flow of the olefin feed was again started.